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Platinum diimine-dithiolate complexes as a new class of photoconducting compounds for pristine photodetectors: case study on [Pt(bipy)(Naph-edt)] (bipy = 2,2'-bipyridine; Naph-edt = 2-naphthylethylene-1,2-dithiolate)
Platinum diimine-dithiolate complexes as a new class of photoconducting compounds for pristine photodetectors: case study on [Pt(bipy)(Naph-edt)] (bipy = 2,2'-bipyridine; Naph-edt = 2-naphthylethylene-1,2-dithiolate)

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The photconducting properties of platinum diimine-dithiolate complex [Pt(bipy)(Naph-edt)] (1; bipy = 2,2'-bipyridine; Naph-edt = 2-naphthylethylene-1,2-dithiolate) were investigated. DFT calculations on a model assembly with four complex units suggest that the high external quantum efficiency measured on a prototype photodetector correlates with the intermolecular character of electronic excitations in the visible region.

Research on 1,2-dithiolene metal complexes has remained continually active since its inception in the early 1960s by Schrauzer. The intense interest in both homoleptic and heteroleptic 1,2-dithiolene metal complexes stems from their unique combination of optical, conductive, magnetic, and catalytic properties, which results in a wide range of applications in fields as varied as optics, laser Q-switching and mode-locking, superconductors, water photolysing, olefin purification, and bioinorganic chemistry. In recent years, among the various heteroleptic 1,2-dithiolene complexes, researchers’ interest has been especially attracted by diimine-dithiolate metal complexes [M(N=N)(S=S)], due to their wide range of potential applications (N=N = diimine; S=S = 1,2-dithiolate). These systems have been applied to dye-sensitized solar cells (DSSC), nonlinear optics (NLO), photocatalysis, DNA intercalation, and as conducting and magnetic materials or sensors. Such a variety of potential applications arises from their peculiar electronic features. Neutral [M(N=N)(S=S)] complexes of d8 metal ions undergo electronic and photochemical processes, and exhibit large molecular hyperpolarizabilities and room-temperature luminescence in solution. Moreover, their electronic spectra show an intense solvatochromic band in the low-energy region, which is considered to involve the highest occupied molecular orbital (HOMO), a mixture of metal and 1,2-dithiolene π-orbital character, and the lowest unoccupied molecular orbital (LUMO), which is a π'-orbital of the diimine. The resulting ligand-to-ligand (LL') transition or mixed metal/ligand-to-ligand charge-transfer (MMLL') transition, depending on the extent of the metal contribution to frontier molecular orbitals, results in the observed negative solvatochromism, since the involved excited state is less polar or polarized in the opposite direction with respect to the ground state.

Besides the aforementioned use of [M(N=N)(S=S)] complexes as active layers in DSSC, the applications of these systems in optoelectronics have scarcely been tapped. Camerel and co-workers recently reported on the preparation of ambipolar discotic liquid crystals built around platinum diimide-dithiolate cores, while the photodetection properties of [Pt(dmeb)(bdt)] were investigated in a Schottky-type device but the external quantum efficiency was not quantified. Following our previous studies on platinum diimine-dithiolate complexes and pursuing our interest in photoconducting bis(1,2-dithiolene) metal complexes, we describe here the development of a photodetector with response in the visible region based on the complex [Pt(bipy)(Naph-edt)] (1; bipy = 2,2'-bipyridine, Naph-edt = 2-naphthylethylene-1,2-dithiolate). Compound 1 (inset in Fig. 1) was synthesized through the reaction between [Pt(bipy)Cl2] and the ligand Naph-edt, generated in situ by treating the corres-
The cyclic voltammogram of 1 in DMSO solution exhibits two one-electron redox waves falling at $-1.727$ and $-0.135$ V vs. Fe$^+/\text{Fc}$, corresponding to its reduction to monoanionic and oxidation to monocationic species, respectively (Fig. S1 in ESI†). No further oxidation is observed in the explored potential range ($-2.0$–$0.5$ V vs. Fe$^+/\text{Fc}$).

Solid-state diffuse reflectance spectra recorded at room temperature for 1 show a maximum in the visible region at 600 nm (Fig. S7 in ESI†). In solution, the visible band displays a remarkable negative solvatochromism, with absorption maxima falling in a range of about 150 nm depending on the solvent ($\lambda_{\text{max}}$ = 600 and 750 nm in MeCN and toluene, respectively; Fig. S2 in ESI†). The stability of 1 over time toward dioxygen photooxidation46 and under continued irradiation was tested (see Experimental Section and Fig. S8 in ESI†). A photoconductive device based on 1 was fabricated by casting a sonicated CH$_2$Cl$_2$ suspension of the complex on a hot quartz substrate with microlithographically defined, interdigitated gold electrodes (interelectrode spacing $L$ = 6 $\mu$m, equivalent width 15 mm), thus obtaining a metal–semiconductor-metal lateral structure (Fig. 1). The device dark current was in the range of few $\mu$A for an applied voltage of 40 V (Fig. S3 in ESI†). The device was irradiated with light pulses lasting 1 s (period 10 s) by a set of light emitting diodes (LEDs) differing in their wavelength (350–800 nm), and the resulting photocurrents were measured by applying an external bias voltage $V_{\text{BIAS}}$ = 60 V and measuring the photocurrent by means of a transimpedance amplifier connected to an oscilloscope. As shown by the external quantum efficiency (EQE) spectrum displayed in Fig. 2, the responsivity of the device and the diffuse reflectance spectrum of 1 (Fig. 3) are in very good agreement, with EQE values peaking about 50% at 600 nm, so that the device acts as an intrinsic wavelength-selective photodetector. This EQE value is not only by far larger than that measured for all the other photodetectors based on pristine homolectic bis(1,2-dithiolen)-metal complexes tested in the past, at best reaching about 1%,$^{38-43}$ but it is also very high in the framework of organic electronics. In fact, organic and organometallic compounds usually display absorption-induced excitations with relatively high binding energies, thus resulting in poor EQE in light harvesting devices; to overcome this, the absorption moiety is usually blended with other species in order to produce distributed heterointerfaces in so-called Donor–Acceptor (DA) blends.$^{47-49}$ In this case, we have obtained a fairly high EQE employing 1 as a pristine (not blended) photoactive material. This is indeed advantageous because DA blends require a fine tuning of the layer morphology to ensure bicontinuous conductive paths for photogenerated charge carriers, while maintaining a large density of heterointerfaces. On the contrary, a single-component, pristine layer is by far easier to deal with and to be optimized.

To rationalize the performance of the photodetector, and to correlate it with the heteroleptic ligand structure, theoretical calculations were performed on complex 1 at the density functional theory (DFT)$^{50}$ level (PBE0 functional,$^{51}$ def2-SVP$^{52,53}$ basis set for C, H, N, S; CRENBL BS$^{54}$ with relativistic effective core potentials$^{55}$ for Pt). The optimized geometry of 1 shows the metal coordinated in a square-planar fashion, with average Pt–S and Pt–N bond distances of 2.263 and 2.046 Å, respectively. The complex is completely planar with the naphthyl substituent tilted by about 31° with respect to the molecular plane (Tables S1, S2 and Fig. S4 in ESI†). The typical composition of the Kohn–Sham (KS) frontier molecular orbitals (MOs) for

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**Fig. 1** Sketch of the planar photodetector prototype.

**Fig. 2** External quantum efficiency (EQE) spectrum (350–820 nm) recorded for the photoconductive device based on 1 and dark-field optical microscopy image (1000x magnification) of the complex cast on the lithographed quartz substrate.

**Fig. 3** Normalized solid-state diffuse reflectance spectrum of 1 (300–1300 nm) and TD-DFT main ($\lambda \geq 0.005$ nm) singlet monoelectronic vertical transitions calculated for 2 (300–850 nm).
[Pt(N^N)(S^S)] complexes is observed at the ground-state (GS), the HOMO being predominantly localized on the 1,2-dithiolato ligand (80%) and the LUMO on the bipyridine moiety (84%), with a similar contribution from the central metal ion to both orbitals (6%; Fig. S5 in ESI†). Time-dependent DFT (TD-DFT) calculations carried out on 1 confirm that the peculiar low-energy absorption can be attributed to the S_0 → S_1 vertical transition, which is in turn assigned to the HOMO–LUMO dithiolate → diimmine one-electron excitation (71%).

Given the localization of the frontier MOs on the two ligands discussed above (Fig. S5 in ESI†), and the small contribution of the atomic orbitals of the metal ion to both KS-MOs, the transition can be considered a LL′CT process, accounting for the typical negative solvatochromism observed experimentally for this absorption (Fig. S2 in ESI†).27–29

In order to get a deeper insight into the photoconduction mechanism, an assembly including four interacting units of complex 1 (2, Fig. S6 in ESI†) was chosen as a simplified model to simulate the intermolecular interactions between complex molecules of 1 in the solid state. After a series of preliminary calculations aimed at establishing the more stable mutual orientation for the complex molecules (see ESI† for more details), the structure of 2 was optimized starting from a conformation featuring the [Pt(bipy)(Naph-edt)] complex units in a slipped head-to-tail fashion (Table S3 and Fig. S6 in ESI†).

The quasi-planar (NN)Pt(SS) cores of neighbouring complex molecules are located above each other, with the naphthyl substituents protruding laterally. Average interplanar separations of 3.64 Å are calculated between the metal cores, which are shifted with respect to each other by 2.3–2.5 Å, resulting in average Pt–Pt distances of 4.35 Å. The average metric parameters within each complex molecule are very close to those calculated for the isolated complex 1 (Table S2 in ESI†).35

TD-DFT calculations carried out on 2 indicate that the broad band at about 600 nm in the solid-state diffuse reflectance spectrum of 1 (Fig. 3 and Fig. S7 in ESI†) should be attributed to a series of transitions, such as S_0 → S_7 and S_0 → S_8 (Fig. 3), corresponding to one-electron vertical excitations from occupied KS-orbitals localized on one complex molecule to unoccupied ones localized on an adjacent complex, retaining a dithiolate → diimmine CT character (Fig. 4 and Fig. S9 in ESI†). These findings suggest that the high-yield photoconducting behaviour observed for compound 1 in the solid state might be attributed to the effective photocharge generation resulting from the intermolecular character of one-electron excitations in the visible region of the electromagnetic spectrum.

Conclusions

In conclusion, diimine-dithiolate Pt^II complexes [Pt(N^N)(S^S)] were attested to be a promising novel class of coordination compounds for the production of pristine photodetectors. This high potential is supported by several reasons. First, [Pt(N^N)(S^S)] complexes feature high photochemical and thermal stabilities in the solid state, rarely encountered among photoactive materials. In addition, the energy of the low-energy transition can be chemically fine-tuned by a suitable choice of the S^S and N^N ligands, since their nature directly affects the energies of the HOMO and the LUMO, respectively. From a technological point of view, casting the complexes from organic solvent solutions allows to directly deposit the active complexes on substrates of any extension and shape and to produce devices straightforwardly on the surface of optical elements, such as beam splitters and fibre-optical-cleaved surfaces.

Further studies are ongoing in our laboratory aimed at extending the findings on complex 1 to a library of related diimine-dithiolate Pt^II complexes and investigating more in depth the structure–property correlation between photogeneration yield and heteroleptic complex character.

Conflicts of interest

There are no conflicts to declare.

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